APPENDIX TO THE SEARCH REPORT ON
EUROPEAN PATENT APPLICATION NO. EP 99,109,597

This appendix indicates the members of the patent families of the patent documents listed in the above-mentioned European search report.
The information on the family members corresponds to the status of the files at the European Patent Office on September 7, 1999.
This data is only meant for information purposes and is non-binding.

Patent document listed in the search report	Date of publication	Member(s) of the patent family	Date of publication
WO 9,318,094 A	September 16, 1993	BR 9,306,018 A	November 18, 1997
		EP 0,629,222 A	December 21, 1994
		FI 944,049 A	September 2, 1994
		HU 68,026 A, B	May 29, 1995
		JP 7,504,457 T	May 18, 1995
		KR 149,206 B	October 1, 1998
		SG 49,195 A	May 18, 1998
US 3,245,820 A	April 12, 1966	none	

For further details about this appendix, see the Official Gazette of the European Patent Office, No. 12/82.

Translation: Language Services Unit
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July 27, 2000

European Patent Office

EUROPEAN SEARCH REPORT

Application Number: EP 99,109,597

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.^{6})
A	WO 93 18094 A (CABOT CORPORATION) September 16, 1993 * Page 19, line 10 through line 14; Tables 2-2 * ---	1-4	C09C1/56 C09C1/54
A	U.S. 3,245,820 A (COLUMBIAN CARBON COMPANY) April 12, 1966 * The entire document * ---	1-4	

TECHNICAL FIELDS SEARCHED (Int. Cl.^{6}): C09C

The present search report has been drawn up for all claims

Place of search:	Date of completion of the search:	Examiner:
The Hague, The Netherlands	September 7, 1999	Luethe, H.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons
&: member of the same patent family, corresponding document

Patent Claims

1. Carbon black that has been after-treated by oxidation,
   characterized in that
   its content of volatile components is more than 10% by weight, preferably more than 15% by weight, relative to its total weight, and in that the ratio of its CTAB surface area to the iodine number is greater than 2 m^2/mg.

2. Carbon black according to Claim 1,
   characterized in that
   the ratio of its CTAB surface area to the iodine number is higher than 4 m^2/mg.

3. Carbon black that has been after-treated by oxidation,
   which can be obtained by oxidizing a gas black with ozone.

4. Use of the carbon blacks according to one of the preceding claims in paints, printing inks and in other inks for mechanical and manual typewriters and drawing instruments.

Application example:

[0035] A special advantage of the types of carbon black according to the invention is the fact that they can be easily dispersed in water and the high stability of such a dispersion. In order to examine this behavior, so-called settling tests were conducted with the carbon black according to the invention and with commercially available comparative types of carbon black. For this purpose, 1 gram of carbon black was dispersed in 99 mL of water, without a wetting agent and with ultrasound for a period of 5 minutes and subsequently the settling of the dispersed carbon black was observed. The glass beakers used for this purpose had a volume of 150 mL and a diameter of 5 cm. Already after 15 minutes, the carbon black not treated with ozone displayed a settling of the carbon black. A clear layer free of carbon black formed at the upper edge of the liquid surface. Specifically, the settling behavior shown below in Table 4 occurred.

Table 4

Settling behavior of various types of carbon black				
Carbon black		Oxidation with	Volatile content [wgt.-%]	Settling after 15 minutes [cm]
SS 550	F [1]	NO_2	2.5	1
FW 200	G [2]	NO_2	24.0	0.5
Printex 90	F	–	1	1
Printex U	G	–	5	0.25
FW1	G	–	4.3	0.5
FW1	G	ozone	15	0

[1] F = furnace carbon black
[2] G = gas black

[0036] In the case of gas black FW1 oxidized with ozone according to the invention, no settling of the carbon black can be seen, even after a week.

obtained no longer constitute a measure of the surface area. However, they are suitable to provide information – in addition to the content of volatile components – about the type of the surface modification brought about by the oxidation treatment.

[0033] In the case of the highly oxidized types of carbon black, the M_y value rises to 328. As the degree of oxidation rises, the composition of the surface oxides also changes. The carboxyl groups and quinones increase markedly, while the phenolic groups and basic oxides diminish. The content of lactols remains virtually unaltered.

Table 3

Analytical characteristic data of types of carbon black oxidized with ozone								
Property	Unit	Duration of treatment of FW 1 with ozone [h]						FW 200
		0	1	2	4	8	16	
Carbon black characteristic numbers								
CTAB	m²/g	236	246	269	311	306	361	485
Iodine number	mg/g	239	198	126	66	67	30	255
CTAB/iodine	m²/g	0.99	1.24	2.14	4.71	4.57	12.03	1.90
BET	m²/g	264						
M_y value			279	281	292	295	328	
DIN color intensity		104	106	102	92	92	82	91
Oil consumption	g/100 g	995	855	560	390	540	295	620
Volatile content	wgt.-%	4.3	7.2	10.6	16.0	16.4	22.7	24.0
pH value		4.4	3.8	3.3	3.1	3.0	2.9	2.8
Surface oxides								
Carboxyl groups	mmol/kg	59	97	228	525	550	922	981
Lactols	mmol/kg	50	78	50	50	38	55	78
Phenols	mmol/kg	94	94	60	63	68	23	261
Quinones	mmol/kg	100	175	506	1012	1132	1445	1208
Basic oxides	mmol/kg	59	38	0	0	0	0	0

[0034] The gas black FW 200 not oxidized with ozone exhibits a completely different ratio of the CTAB surface area to the iodine number, which can be ascribed to the different composition of the surface oxides.

[0028] The ozone concentration that needs to be reached depends on the generator voltage, on the quantity of carrier gas and on its oxygen content. At a generator voltage of 16 kV, a maximum of 12 grams of ozone per hour can be reached when air is used and a maximum of 25 grams of ozone per hour when oxygen is used.

Example 1:

[0029] The gas black FW 1 was oxidized for varying periods of time in the apparatus shown in Figure 1 and subsequently analyzed in terms of the technical properties of the carbon black.

[0030] For every oxidation experiment, the ozone generator was operated at a constant air volume of 310 NL/h. In each case, the fluidized bed was loaded with 200 grams of carbon black. For all of the experiments, the reaction temperature lay within the range from 20°C to 30°C [68°F and 86°F]. Table 3 shows the results obtained for FW 1 with different treatment times in comparison to untreated FW 1 and to the commercially available oxidized gas black FW 2000.

[0031] According to Table 3, the following relationships were found with respect to the duration of the ozone oxidation:

- increase in the volatile content;
- drop in the pH value;
- increase in the CTAB surface area;
- decrease in the iodine number;
- decrease in the DIN color intensity;
- decrease in the oil consumption;
- marked change of the surface oxide composition.

[0032] The changes found in the CTAB surface area and iodine number do not mean that the ozone oxidation changes the particle size and thus the surface area, particularly since these are opposite effects. Rather, by modifying the carbon black surface area, the adsorption of iodine and CTAB is influenced to such a great extent that the numbers

[0023] A remarkable aspect of this list is the commercially available gas black FW 200. It is a gas black that has not been oxidized with ozone. In spite of its high content of volatile components, it does not exhibit the required ratio of CTAB to iodine.

[0024] The invention will be elaborated upon with reference to the following examples. The figures show the following:

Figure 1: Apparatus used for the oxidation of carbon black with ozone

[0025] Figure 1 shows a suitable fluidized-bed apparatus for the batchwise oxidation of carbon black with ozone. It consists of a vertical cylindrical treatment tank (1) that, at its lower end, has a fluidizing part consisting of a jacket (2) in the shape of a truncated cone that runs downwards from the cylindrical cross section, of a conical displacement element (3) that tapers upwards and that is inserted into the truncated cone and of at least one feed tube (4) for the treatment gas that opens essentially tangentially into the deepest place of the fluidizing part. Above the treatment tank (1), there is a relaxation part (5) with an outlet tube (6) for the flue gas. The carbon black feed nozzles (8) are used to feed carbon black into the treatment tank. The numeral (9) refers to a sensor that serves to regulate the height of the fluidized bed. For purposes of generating ozone, the treatment gas (air or oxygen) passes through the ozone generator (7) prior to entering the treatment tank. The treatment tank has an inner diameter of 8 cm and a height of 1.5 m.

[0026] The apparatus shown in Figure 1 is used to oxidize carbon black batchwise. By configuring the fluidized bed accordingly, however, it is possible to achieve continuous operation of the process.

[0027] An ozone generator with the following performance specifications was employed for the oxidation experiments.

operating pressure:	maximum of 0.6 bar
quantity of carrier gas:	maximum of 600 L/h
cooling water:	40 L/h (15°C [59°F]
operating temperature:	maximum of 35°C [95°F]
generator voltage:	16 kV

bon black dispersion makes the carbon black types according to the invention particularly well-suited for use in paints, printing inks and as inks for mechanical and manual typewriters and drawing instruments, for example, as inks for ink-jet printers, felt-tip pens and ball-point pens.

[0022] The carbon black types according to the invention can be obtained by means of the ozone oxidation of gas blacks. Furnace black types are not suitable as the initial carbon black since their content of volatile components cannot be raised above 7% to 8% by weight, even by means of ozone oxidation. Corresponding measurements with commercially available types of pigment carbon black made by various manufacturers can easily show that the claimed property combination was not known up until now. Such measurements can be found in Table 2.

Table 2

Properties of commercially available types of pigment carbon black				
Carbon black	Volatile components [wgt.-%]	CTAB surface area [m²/g]	Iodine adsorption [mg/g]	CTAB/iodine [m²/mg]
Cabot				
Monarch 1300	11.7	363	479	0.76
Monarch 1000	12.4	255	314	0.81
Mogul L	4.8	132	110	1.20
Columbian				
Raven 5000 UII	15.2	346	302	1.15
Raven 1255	6.2	119	73	1.63
Degussa				
FW 200	24.0	485	255	1.90
FW 1	4.3	236	239	0.99
Printex U	5	99	63	1.57
Printex 90	1	250	350	0.71
SS 550	2.5	120	101	1.19

[0017] The iodine adsorption, also called the iodine number, is a third method for characterizing the surface area of carbon black types. The iodine number is determined according to ASTM D-1510. It is strongly influenced by surface groups and adsorbed PAHs. Consequently, the adsorption value measured in mg/g is not converted into m^2/g. Normally, the iodine adsorption in only indicated for carbon black types with volatile components below 1.5% by weight and with a toluene extract under 0.25% by weight. In view of its sensitivity to the volatile surface groups, however, the iodine adsorption can be utilized as yet another characterization possibility for oxidized types of carbon black with a high fraction of volatile components.

[0018] The objective of the present invention is to provide carbon blacks that can be used for paints and printing inks, and that stand out for an improved dispersion behavior in water-based binder systems and for an improved long-term stability on the part of the paints and printing inks made with these types of carbon black.

[0019] This objective is achieved by means of a carbon black that has been after-treated by oxidation, which is characterized in that its content of volatile components is more than 10% by weight, preferably more than 15% by weight, relative to its total weight, and in that the ratio of its CTAB surface area to the iodine number is greater than 2 m^2/g. Preferably, the ratio of the CTAB surface area to the iodine number is higher than 4 m^2/g. In addition, these types of carbon black do not exhibit any measurable concentration of basic surface oxides.

[0020] In this context, the CTAB surface area and the iodine number are measured in accordance with the above-mentioned ASTM standards. The important aspect here is that, prior to the measurement, the carbon black types do not undergo any thermal treatment for the desorption of the volatile components.

[0021] It has been found that the required property combination consisting of volatile components and a certain minimum ratio of the CTAB surface area to the iodine number causes carbon black to disperse in water very easily and causes this dispersion to remain stable over the course of several days without the need for the addition of a wetting agent or dispersion additive. This high level of storage stability on the part of the aqueous car-

[0013] For the reasons cited, pigment carbon black is generally after-treated by oxidation in order to raise its content of volatile components. Oxidants that can be used are nitric acid, nitrogen dioxide and, to a lesser extent, ozone. The contents of volatile components and the pH values listed in Table 1 can be raised by means of oxidative after-treatment. In this context, the oxidation behavior is highly dependent on the production process of the carbon black. In the case of furnace black types, the content of volatile components can only be raised to about 6% by weight. For instance, U.S. 3,565,657 reports on the oxidation of furnace black types with nitric acid. The highest content of volatile components cited in this patent is 7.6% by weight.

[0014] Several patents describe the attempt to replicate the advantageous properties of gas black types – properties that stem from their high volatile fraction – by means of the ozone-treatment of furnace black types. These include the following patents: U.S. 3,245,820, U.S. 3,364,048 and U.S. 3,495,999. According to U.S. 3,245,820, the ozone treatment made it possible to increase the volatile fraction of the furnace blacks to 4.5% by weight.

[0015] Another important property of the carbon blacks is their specific surface area, which is determined by means of various adsorption methods. When the nitrogen surface area is determined (BET surface area according to DIN 66132), the carbon black surface is first loaded with nitrogen molecules, whereby the known space requirement of the nitrogen molecule makes it possible to make a conversion to m^2/g. Since the small nitrogen molecule can also penetrate into the pores and gaps found in the carbon black, this method also involves the inner surface area of the carbon black types.

[0016] A greater space requirement than for nitrogen is needed for cetyl trimethyl ammonium bromide (CTAB). Therefore, the CTAB surface area (measurement according to ASTM D-3765) comes closest to the determination of the geometrical surface area without pores. For this reason, the CTAB surface area correlates very closely with the particle size and thus allows conclusions to be drawn about the applications-technology behavior of the carbon blacks.

Table 1

Property	Furnace black	Gas black	Flame black
color depth M_Y	210 - 270	230 - 300	200 - 220
color intensity IRB3=100	60 - 130	90 - 130	25 - 35
oil consumption [g/100g]	200 - 500	400 - 1100	250 - 400
DBP adsorption [mL/100g]	40 - 200		100 - 120
particle size [nm]	10 - 80	10 - 30	110 - 120
volatile components [wgt.-%]	0.5 - 1.5	4 - 6	1 - 2.5
pH value	8 - 10	4 - 6	6 - 9

[0009] Important properties of a paint or of a printing ink in terms of applications technology are the stability of the carbon black dispersion in the binder system (storage stability) and the rheologic behavior of the paint or of the printing ink (viscosity and thixotropy). These properties are greatly influenced by the chemical nature of the surface of the carbon black.

[0010] The surface chemistry of the carbon black is very dependent on the production process selected. In the case of the furnace black method, the carbon black is formed in a strongly reducing atmosphere whereas, in the gas black method, the atmospheric oxygen has free access to the zone where the carbon black is being formed. Consequently, already immediately after their production, the gas black types have a considerably higher content of surface oxides than the furnace black types do.

[0011] The surface oxides are essentially carboxyl groups, lactols, phenols and quinones which lead to an acidic reaction of aqueous carbon black dispersions. To a lesser extent, the carbon blacks also have basic oxides on the surface. The surface oxides make up the so-called volatile components of the carbon black, since they can be desorbed from the carbon black surface by annealing the carbon black at 950°C [1742°F] (DIN 53552).

[0012] The content of volatile components exerts a decisive influence on the dispersability of the carbon blacks, particularly in aqueous systems. The higher the content of volatile components in the carbon blacks, the less the hydrophobic character of the carbon blacks and thus the more easily they can be dispersed in water-based binder systems.

[0005] The apparatus for making flame black consists of a cast-iron tray that holds the liquid or optionally melted raw material and of an exhaust hood lined with refractory material. The air gap between the tray and the exhaust hood as well as the negative pressure in the system serve to regulate the air feed and thus the properties of the carbon black. The heat radiation brought about by the exhaust hood causes the raw material to be vaporized and partially burn, although most of it is converted into carbon black. In order to separate the carbon black, the process gases containing carbon black are passed through a filter after they have cooled off.

[0006] With the gas black method, the carbon black raw material is first vaporized into a carrier-gas flow containing hydrogen and then burned in numerous small flames underneath a cooled roller. Some of the resultant carbon black precipitates on the roller while the rest is discharged together with the process gases and is separated out in a filter.

[0007] The properties that are important for evaluating pigment carbon blacks are the color depth M_Y (according to German standard DIN 55979), the color intensity (preparation of a carbon black paste according to DIN EN ISO 787/16 and evaluation according to DIN EN ISO 787/24), the oil consumption (according to DIN EN ISO 787/5), the volatile components (according to DIN 53552), the structure, measured as DBP absorption (according to DIN 53601 or ASTM D2414), the mean size of the primary particles (by means of the evaluation of electron-microscopic images) and the pH value (according to DIN EN ISO 787/9 or ASTM D1512).

[0008] Table 1 shows the property ranges that can be attained for various types of pigment carbon black by means of the above-mentioned production processes. The data in Table 1 was compiled from technical publications by various carbon black manufacturers pertaining to the characteristic numbers of carbon blacks that had not been after-treated by oxidation.

Description

[0001] The invention relates to carbon black that has been after-treated by oxidation in order to be used as a pigment in paints, printing inks and other inks, for example, in ink-jet printers.

[0002] Due to its outstanding properties, it is primarily carbon black that is used as the black pigment in paints and printing inks. A wide selection of types of carbon black with varying properties is available. Various methods are employed in order to produce pigment carbon black. The most frequent is production by means of the oxidative pyrolysis of carbon black raw materials containing carbon. In this process, the carbon black raw materials are incompletely burned at high temperatures in the presence of oxygen. This class of production processes for carbon black includes, for instance, the furnace black method, the gas black method and the flame black method. Primarily polynuclear aromatic carbon black oils are employed as the carbon black raw materials containing carbon.

[0003] In the furnace black method, the incomplete combustion takes place in a reactor lined with highly refractory material. For this purpose, a fuel-air mixture is burned in a pre-combustion chamber in order to generate a flow of hot flue gases into which the carbon black raw material is sprayed or injected. The carbon black thus formed is quenched when water is injected into the reactor and it is then separated from the gas flow. The furnace black method allows the production of carbon black types having a very broad spectrum of the technical properties needed for carbon black applications.

[0004] The flame black method and the gas black method are important alternatives to the furnace black method. They yield carbon blacks whose properties can at times overlap with the technical properties of carbon black that can be achieved by means of the furnace black method, in addition to which they also give access to types of carbon black that cannot be made by means of the furnace black method.

TRANSLATION

[19] Europäisches Patentamt
European Patent Office
Office européen des brevets

[11] Publication number:
EP 0,969,052 A1

[12] EUROPEAN PATENT APPLICATION

[43] Date of publication:
January 5, 2000 Bulletin 2000/01

[51] Int. Cl.[7]: C09C 1/56, C09C 1/54

[21] Application number: 99,109,597.7

[22] Date of filing: May 14, 1999

[84] Designated Contracting States:
AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LI, LU, MC, NL, PT, SE

Designated Extension States:
AL, LT, LV, MK, RO, SI

[30] Priority:
May 29, 1998
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[54] **Carbon black after-treated by oxidation.**

[57] The invention relates to carbon black that has been after-treated by oxidation. It is characterized in that its content of volatile components amounts to more than 10% by weight relative to its total weight and in that the ratio of its CTAB surface area to the iodine number is greater than 2 m^2/mg. The carbon black according to the invention is preferably employed as a pigment carbon black in the manufacture of water-based paints, printing inks and other inks for mechanical and manual typewriters and drawing instruments. The combination of properties imparts the carbon black with excellent dispersability in water-based binder systems. The paints, printing inks and other inks made with it exhibit excellent storage stability.

EP 0,969,052 A1